

## TITLE OF INVENTION

### VISCOSITY INDEX IMPROVER AND LUBE OIL CONTAINING THE SAME

#### BACKGROUND OF THE INVENTION

##### 1. Field of the Invention

This invention relates to a viscosity index improver (hereinafter referred to as VII or VI improver). More particularly, it relates to a VII for lube oils, such as gear oils, transmission fluids, traction oils, hydraulic oils and engine oils.

##### 2. Description of the Prior Art

As VI improvers to improve viscosity index (herein-after referred to as VI) of lube oils, there have been known heretofore copolymers of C<sub>1</sub>-24 alkyl (meth)acrylates and a hydroxyalkyl (meth)acrylate (for instance, EP 0570093). The term "(meth)acrylate" represents acrylate and/or methacrylate and also "C<sub>1</sub>-<sub>24</sub>alkyl" represents alkyl group containing 1-24 carbon atoms; and similar expressions are used hereinafter.

#### SUMMARY OF THE INVENTION

It is an object of the present invention to provide a VII capable of imparting an improved VI to a lube oil.

It is another object of the invention to provide a VII having an improved shear stability.

It is still another object of this invention to provide a VII capable of imparting an improved low temperature viscosity characteristics to a lube oil.

It is yet another object of the present invention to provide a high VI lube oil having an improved shear stability and low temperature viscosity.

It is further object of the present invention to provide an automotive lube oil capable of meeting fuel economy requirement and long life of an automobile.

Briefly, these and other objects of this invention as hereinafter will become more readily apparent have been attained broadly by a VII, which comprises an oil-soluble copolymer (A) comprising units of a monomer (a) represented by the general formula (1), units of at least one monomer (b) selected from the group consisting of C<sub>8-17</sub>alkyl (meth)-acrylates (b1) and straight-chain C<sub>18-24</sub>alkyl (meth)-acrylates (b2), and units of an unsaturated monomer (c) having at least one group selected from the group consisting of hydroxyl, amide and carboxyl groups.



In the formula (1), R<sup>1</sup> is H or CH<sub>3</sub>, A is a C<sub>2-4</sub>alkylene group, n is 0 or an integer of 1-20, and R is a branched C<sub>18-36</sub>alkyl group, free from any polymethylene group containing more than 16 carbon atoms.

The copolymer (A) usually contains 5-90% of units of (a), 5-90% of units of (b), 5-50% of units of (c). In the above and hereinafter, % represents % by weight, unless otherwise specified.

The copolymer (A) generally has a weight-average molecular weight (hereinafter referred to as M<sub>w</sub>) of at least 3,000.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

##### Monomer (a)

In the formula (1), n is preferably at most 10, more preferably at most 5, particularly 0.

Suitable C<sub>2-4</sub>alkylene groups A include ethylene, propylene, and 1,2-, 2,3-, 1,3- and 1,4-butylene groups; as well as combinations of two or more of these groups, in case of n being at least 2, which groups may be distributed random-wise and/or block-wise whithin the polyoxyalkylene moiety -(A-O)<sub>n</sub>- . Among alkylene groups, preferred

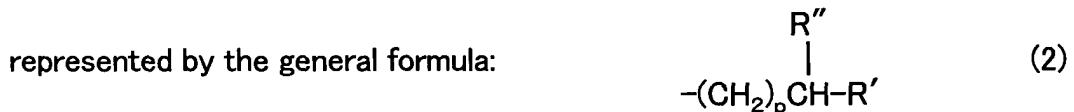
are ethylene, propylene and combinations of them.

R<sup>1</sup> is preferably methyl group.

Branched alkyl group R contains preferably 20–32, particularly 20–28, more particularly 20–24, most preferably 24 carbon atoms, in regard of VI, and low viscosity even at low temperature. Branched alkyl group R may contain a polymethylene group containing generally at most 16, preferably 2–14, particularly 4–14, more particularly 6–14, most preferably 10–12 carbon atoms, in regard of VI and low temperature viscosity. The number of carbon atoms in the polymethylene group contains a carbon atom in methyl end group.

Branched alkyl group R have usually 1–17, preferably 1–12, particularly 1–6 branchings, and most preferably 1 branching.

Suitable branched alkyl groups of R include ones



In the formula (2), p is 0 or an integer of 1–15, and R' and R'' are independently selected from the group consisting of straight-chain C<sub>1–16</sub>alkyl groups and branched C<sub>3–34</sub>alkyl groups.

Examples of suitable branched alkyl group R include 1) ones having a C<sub>15–16</sub> polymethylene group, such as 1-C<sub>1–15</sub>alkyl-hexadecyl groups (e.g. 1-octylhexadecyl) and 2-C<sub>1–15</sub>alkyl-octadecyl groups (e.g. 2-ethyloctadecyl, 2-tetradecyl-octadecyl and 2-hexadecyloctadecyl); 2) ones having a C<sub>13–14</sub>polymethylene group, such as 1-C<sub>1–15</sub> alkyl-tetradecyl groups (e.g. 1-hexyltetradecyl, 1-decyltetradecyl and 1-undecyl-tridecyl) and 2-C<sub>1–15</sub>alkyl-hexadecyl groups (e.g. 2-ethyl-hexadecyl and 2-dodecylhexadecyl); 3) ones having C<sub>10–12</sub>polymethylene group, such as 1-C<sub>1–15</sub>alkyl-dodecyl groups (e.g. 1-octyldodecyl) and 2-C<sub>1–15</sub>alkyl-dodecyl groups (2-hexyldodecyl and 2-octyldodecyl), 2-C<sub>1–15</sub>alkyl-tetradecyl groups (e.g. 2-hexyltetradecyl and 2-decyltetradecyl); 4) ones having C<sub>6–9</sub>polymethylene group, such as 2-C<sub>1–15</sub>alkyl-decyl

groups (e.g. 2-octyldecyl and 2,4-di-C<sub>1-15</sub>alkyl-decyl groups (e.g. 2-ethyl-4-butyl-dodecyl group); 5) ones having C<sub>1-5</sub>polymethylene group, such as 2-(3-methyhexyl)-7-methyl-decyl and 2-(1,4,4-trimethylbutyl)-5,7,7-trimethyl-octyl groups; 6) and mixtures of two or more branched alkyl groups, such as alkyl residues of oxoalcohols corresponding to propylene oligomers (from hexamer to undecamer), ethylene/propylene (molar ratio 16/1 – 1/11) oligomers, iso-butene oligomers (from pentamer to octamer), C<sub>5-17</sub>  $\alpha$ -olefin oligomers (from dimer to hexamer) and the like.

Among these, preferred are those of the formula (2), wherein p is 0 or 1 (particularly 1), and R' and R'' are independently selected from the group consisting of straight-chain C<sub>6-16</sub> (particularly C<sub>8-14</sub>) alkyl groups and branched C<sub>6-18</sub> (particularly C<sub>8-14</sub>) alkyl groups. More preferred are 2-alkyl groups, particularly 2-C<sub>8-10</sub>alkyl-C<sub>12-14</sub>alkyl, represented by the formula (2), wherein p is 1, and R' and R'' are straight-chain C<sub>8-10</sub>alkyl and straight-chain C<sub>10-12</sub>alkyl groups, in regard of VI and low temperature viscosity.

Illustrative of suitable monomers (a) are branched alkyl methacrylates, such as 2-octyldodecyl and 2-decyl-tetradecyl methacrylates (hereinafter referred to as O-DM and D-TDM, respectively), and 1-octyldodecyl, 2-hexyl-dodecyl, 2-hexyltetradecyl, 1-hexyltetradecyl, 1-decyl-tetradecyl, 1-undecyltridecyl, 2-ethylhexadecyl, 2-dodecyl-hexadecyl, 2-octyldodecyloxyethyl and 2-decyltetradecyl-oxyethyl methacrylates; as well as corresponding acrylates, such as 2-octyldodecyl and 2-decyltetradecyl acrylates.

Among these, preferred are O-DM and D-TDM.

#### Monomer (b)

Suitable (meth)acrylates (b1) are inclusive of (b11) straight-chain C<sub>8-17</sub>alkyl (meth)acrylates, for example, straight-chain alkyl methacrylates, such as n-dodecyl, n-tetradecyl-, n-hexadecyl and n-octadecyl methacrylates (hereinafter referred to as DDM, TDM, HDM and ODM, respectively), n-octyl, n-nonyl, n-decyl, n-tridecyl and n-

pentadecyl methacrylates, and (meth)acrylates of Ziegler alcohols, and corresponding acrylates, such as n-dodecyl acrylate (hereinafter referred to as DDA); (b12) branched C<sub>8-17</sub>alkyl (meth)acrylates, for instance, i-octyl, 2-ethyl-hexyl, i-nonyl, i-decyl, i-dodecyl, 2-methylundecyl, i-tridecyl, 2-methyldodecyl, i-tetradecyl, 2-methyltridecyl, i-pentadecyl and 2-methyltetradecyl (meth)acrylates; and (b13) (meth)acrylates of a mixture of straight-chain C<sub>6-16</sub>alcohols and branched-chain C<sub>6-16</sub>alcohols, for example, (meth)acrylates of oxoalcohols (such as "NEODOL 23" and "NEODOL 45", produced by Shell Chemical Co., "DOBANOL 23" and "DOBANOL 45", produced by Mitsubishi Chemical Corp., and "OXOCOL 1213" and "OXOCOL 1415", produced by Nissan Chemical Industries, Ltd.). Among these, preferred in regard of VI and low viscosity even at low temperature are C<sub>12-17</sub>(preferably C<sub>12-15</sub>)alkyl (meth)acrylates, more preferred are straight-chain C<sub>12-17</sub>(especially C<sub>12-15</sub>)alkyl (meth)acrylates.

Suitable (meth)acrylates (b2) include, for example, straight-chain C<sub>18-24</sub>alkyl methacrylates, such as n-octadecyl, n-nonadecyl, n-eicosyl, n-docosyl and n-tetracosyl (meth)acrylates. Among these, preferred in regard of VI and low viscosity even at low temperature are n-octadecyl (meth)acrylates.

#### Monomer (c)

Suitable unsaturated monomers (c) include hydroxyl-containing monomers (c1), amide-containing monomers (c2) and carboxyl-containing monomers (c3). Examples of these monomers are as follows.

##### Monomers (c1):

(c11) hydroxyl-containing acrylic monomers, including (c111) (meth)acrylates represented by the general formula:



wherein R<sup>1</sup> and A are the same as in the formula (1) and m is an integer of 1-20 (preferably 1); for example, C<sub>2-4</sub>hydroxyalkyl (meth)acrylates, such as 2-hydroxyethyl methacrylate and 2-hydroxyethyl acrylate (hereinafter referred to as HEMA and HEA,

respectively), and 2-hydroxy-propyl, 3-hydroxypropyl and 2-hydroxyethoxyethyl (meth)-acrylates; and (c112) (meth)acrylates of a polyhydric alcohol having 3-8 hydroxyl groups (for instance, C<sub>3-12</sub>alkane polyols and intramolecular or intermolecular dehydrates thereof, such as glycerol, trimethylolpropane, 1,2,6-hexanetriol, pentaerythritol, sorbitol, sorbitan and diglycerol; and saccharides and glycosides, such as sucrose and methyl glucoside), for example, glycerol mono- and di-(meth)acrylates, trimethylolpropane mono- and di-(meth)acrylates, and sucrose (meth)acrylates; (c12) alkenols, for example, vinyl alcohol, units thereof being obtainable by hydrolysis of units of vinyl acetate; and C<sub>3-12</sub>alkenols, such as propenols (propenyl alcohol and allyl alcohol), butenols (crotyl alcohol, 1-butene-3-ol and 1-butene-4-ol), 1-octenol, 1-undecenol and 1-dodecenol;

(c13) C<sub>4-12</sub>alkenediols, such as 2-butene-1,4-diol;

(c14): hydroxyl-containing C<sub>3-12</sub>alkenyl ethers, for example, C<sub>3-12</sub>alkenyl ethers corresponding to (c12), such as propenyl, (meth)allyl and crotyl ethers, including C<sub>1-6</sub> hydroxyalkyl C<sub>3-12</sub>alkenyl ethers, such as 2-hydroxyethyl propenyl ether; and C<sub>3-12</sub> alkenyl ethers of a polyhydric alcohol as in (c112), such as trimethylolpropane mono- and di-(meth)allyl ethers and sucrose (meth)allyl ethers;

(c15) hydroxyl-containing aromatic unsaturated monomers, such as p-hydroxystyrene; and

(c16) (poly)oxyalkylene ethers of monomers (c11)-(c15), at least one hydroxyl group thereof having been substituted with -O-(AO)<sub>n</sub>-A-OH wherein A and n are the same as in the formula (1).

Among these, preferred are (c12), (c14), (c15), (c16) and (c11), especially (c11). More preferred are HEA and particularly HEMA.

Monomer (c2):

(c21) (meth)acrylamides represented by the general formula:



wherein R<sup>2</sup> and R<sup>3</sup> are independently selected from the group consisting of hydrogen atom, C<sub>1-4</sub>alkyl groups and C<sub>1-4</sub>hydroxyalkyl groups, and R<sup>1</sup> is H or CH<sub>3</sub>; including (c211) unsubstituted and alkyl-substituted acrylamides, for example, acrylamide, methacrylamide (hereinafter referred to as AAm); N-mono-C<sub>1-4</sub>alkyl- and N,N-di-C<sub>1-4</sub>alkyl-substituted (meth)acrylamides, such as (di)methyl, (di)ethyl, (di)i-propyl, (di)n-butyl and (di)i-butyl (meth)acrylamides; and (c212) hydroxyalkyl-substituted acrylamides, for example, N-mono-C<sub>1-4</sub>hydroxyalkyl-, N,N-di-C<sub>1-4</sub>hydroxyalkyl-substituted and N,N-C<sub>1-4</sub>alkyl-substituted (meth)acrylamides, such as N-hydroxymethyl, N,N-dihydroxy-methyl, N,N-di-2-hydroxyethyl, N,N-di-4-hydroxy-butyl and N,N-methyl-hydroxyethyl (meth)acrylamides; as well as (c22) N-vinylcarbonamides, for instance, acyclic N-vinyl-carbonamides, such as N-vinyl-formamide, N-vinylacetoamide, N-vinyl-n- and i-propion-amides and N-vinyl hydroxyaceto-amide; and N-vinyl-lactams, such as N-vinylpyrrolidone.

Among these, preferred are monomers (c211), particularly (meth)acrylamides, more particularly AAm.

#### Monomer(c3):

(c31) unsaturated monocarboxylic acids, such as methacrylic acid (hereinafter referred to as MAA), and acrylic, α-methyl(meth)acrylic, (iso)crotonic and cinnamic acids; (c32) unsaturated dicarboxylic acids and mono-C<sub>1-8</sub>alkyl ester thereof, such as maleic, fumaric, itaconic, citraconic and mesaconic acids, and mono-alkyl maleates, fumarates and itaconates.

Among these monomers (c), preferred in regard of VI and shear stability are (c2) and particularly (c1).

Polymers (A) may further contain units of one or more additional monomers. Suitable additional monomers include, for example, the following monomers (d), (e), (f),

(g), (h) and (i).

Monomer (d): alkyl (meth)acrylates other than (a) and (b):

(d1) C<sub>1–4</sub>alkyl (meth)acrylates, including methyl, ethyl, n– and i–propyl, and n–, i–, sec– and t–butyl (meth)acrylates;

(d2) C<sub>5–7</sub>alkyl (meth)acrylates, such as n–, neo– and iso– pentyl, and n– and iso–hexyl (meth)acrylates; and

(d3) branched C<sub>18–36</sub>alkyl group, having a polymethylene group containing 17 or more carbon atoms, such as 2–methyl–nonadecyl methacrylate (hereinafter referred to as M–NM).

Among these, preferred are (d1) particularly methyl methacrylate (hereinafter referred to as MMA).

Monomer (e): unsaturated C<sub>2–20</sub>hydrocarbons, including

(e1) unsaturated aliphatic C<sub>2–20</sub>hydrocarbon monomers, for example, C<sub>2–20</sub>alkenes, such as ethylene, propylene, (iso)–butene, pentene, heptene, diisobutylene, octene, dodecene and octadecene; and C<sub>4–12</sub>alkadienes, such as butadiene, isoprene, 1,4–pentadiene, 1,6–heptadiene and 1,7–octadiene; (e2) unsaturated alicyclic C<sub>5–20</sub> hydrocarbon monomers, for example, cycloalkenes, such as cyclohexene; (di)cycloalkadienes, such as (di)cyclopentadiene; (bi)cyclic terpenes, such as pinene and limonene; vinyl(di)cycloalkenes, such as vinylcyclohexene; ethylidene(di)cycloalkenes, such as ethylidenebicycloheptene and ethylidene–norbornene; and aromatic ring-containing cycloalkenes, such as indene; and (e3) unsaturated aromatic hydrocarbon monomers, for example, styrene, and homologues thereof, including C<sub>1–20</sub>hydrocaryl–substituted styrenes, such as α–methylstyrene, vinyltoluene, 2,4–dimethylstyrene, 4–ethylstyrene, 4–iso–propylstyrene, 4–butylstyrene, 4–phenylstyrene, 4–cyclo–hexylstyrene, 4–benzylstyrene and 4–crotylbenzene; and C<sub>2–10</sub>alkenylnaphthalenes, such as 2–vinylnaphthalene.

Monomer (f): vinyl ketones, for example, C<sub>1–10</sub>alkyl or C<sub>6–8</sub>aryl vinyl ketones, such as

methyl vinyl ketone, ethyl vinyl ketone and phenyl vinyl ketone.

Monomer (g): epoxy-containing unsaturated monomers, for example, epoxy-containing acrylic monomers, such as glycidyl (meth)acrylates; and epoxy-containing C<sub>2</sub>–C<sub>10</sub>alkenyl (preferably C<sub>3</sub>–C<sub>6</sub>alkenyl) ethers, such as glycidyl (meth)allyl ethers.

Monomer (h): halogen-containing unsaturated monomers, for example, vinyl or vinilidene halides, such as vinyl chloride, vinyl bromide and vinylidene chloride; C<sub>3</sub>–C<sub>6</sub>alkenyl halides, such as (meth)allyl chlorides; and halo-substituted styrenes, such as (di)chlorostyrenes.

Monomer (i): C<sub>1</sub>–C<sub>10</sub>alkyl C<sub>2</sub>–C<sub>10</sub>alkenyl ethers, for example, alkyl vinyl ethers, such as methyl vinyl ether, n-propyl vinyl ether and ethyl vinyl ether, and alkyl (meth)allyl ethers and (iso)propenyl ethers, such as methyl allyl ether and ethyl allyl ether.

Monomer (j): C<sub>2</sub>–C<sub>10</sub>alkenyl C<sub>1</sub>–C<sub>20</sub>carboxylates, for example, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl hexanoate, vinyl heptanoate, vinyl 2-ethylhexanoate and vinyl n-octanoate. Among these, preferred are vinyl acetate and vinyl propionate.

Monomer (k): nitrogen-containing unsaturated monomers, other than (c2):

(k1) amino-containing monomers, containing at least one of primary, secondary and tertiary amino groups:

(k11) aliphatic amino-containing monomers, for example, (k111) mono- and di-alkenyl amines, represented by the general formula: D–NH–D<sup>1</sup>, wherein D<sup>1</sup> is H or D and D is C<sub>2</sub>–C<sub>10</sub>(preferably C<sub>3</sub>–C<sub>6</sub>)alkenyl group, such as (di)(meth)-allyl amines and (iso)crotyl amines; and (k112) amino-containing acrylic monomers, including amino-containing (meth)acrylates, for instance, (mono-C<sub>1</sub>–C<sub>4</sub>alkyl)C<sub>2</sub>–C<sub>6</sub>amino-alkyl methacrylates, such as aminoethyl, aminopropyl methylaminoethyl, ethylaminoethyl, butylaminoethyl and methylaminopropyl methacrylates, di-C<sub>1</sub>–C<sub>4</sub>alkyl-C<sub>2</sub>–C<sub>6</sub>amino-alkyl methacrylates, such as dimethylaminoethyl meth-acrylate and diethylaminoethyl methacrylate (hereinafter referred to as DMAEM and DEAEM respectively), dibutylamino-ethyl and dimethylaminopropyl methacrylates; and amino-containing acrylates corresponding to these methacrylates; as well as amino-containing (meth)acrylamides, corresponding to

these (meth)acrylates;

(k12) amino-containing heterocyclic monomers, for example, (k121) heterocyclic amino-containing acrylic monomers, such as morpholino-C<sub>2</sub>-4alkyl (meth)acrylates, e.g. morpholino-ethyl methacrylate (hereinafter referred to as MOEM) and morpholinoethyl acrylate; and (k122) vinyl-substituted heterocyclic amines, such as vinylpyridines (e.g. 4- and 2-vinylpyridines), N-vinylpyrrole and N-vinylpyrrolidine;

(k13) aromatic amino-containing monomers, for example, amino-styrenes, such as aminostyrenes, (di)methylamino-styrenes, phenylaminophenyl(meth)acrylamides, such as 4- and 2-phenylaminophenyl(meth)acrylamides; and  
as well as

(k14) salts of (k11)-(k13), for instance, hydrochlorides, phosphates and C<sub>1</sub>-8alkanoates;

(k2) quaternary ammonium-containing monomers, for example, quaternary ammonium salts, obtainable by quaternarization of (k11)-(k13) with one or more (ar)alkylating agents, such as C<sub>1</sub>-8alkyl halides (e.g. methyl chloride), benzyl halides (e.g. benzyl chloride), di-C<sub>1</sub>-2alkyl sulfates (e.g. dimethyl and diethyl sulfates) and di-C<sub>1</sub>-2alkyl carbonates (e.g. dimethyl carbonate) or by quaternarization of (k14) with one or more C<sub>2</sub>-4alkylene oxides, such as ethylene oxide and propylene oxide; and

(k3) nitrile or nitro group-containing monomers, for example, (meth)acrylonitriles, nitrostyrenes, and the like.

Monomer (m): unsaturated esters other than (a) (c) and (d), including unsaturated dicarboxylic acid esters (such as maleic, fumaric, itaconic, citraconic and mesaconic esters), corresponding to (meth)acrylates (a) (c) and (d), such as C<sub>1</sub>-40hydrocarbyl (e.g. alkyl, cycloalkyl and aralkyl) esters (preferably C<sub>1</sub>-20alkyl esters), for example, dimethyl, diethyl and dioctyl maleates, as well as fumarates and itaconates corresponding to these maleates.

## MONOMER COMPOSITION IN COPOLYMER (A)

In regard of VI, shear stability and low viscosity even at low temperature, copolymers (A) contain units of monomers in such an amount, based on the total weight of monomers, as follows.

	<u>usually</u>	<u>preferably</u>	<u>more preferably</u>	<u>particularly</u>
units of (a)	$\geq 5\%$ , $\leq 90\%$	$\geq 10\%$ , $\leq 70\%$	$\geq 20\%$ , $\leq 60\%$	
units of (b)	$\geq 5\%$ , $\leq 90\%$	$\geq 10\%$ , $\leq 70\%$	$\geq 20\%$ , $\leq 60\%$	
units of (c)	$\geq 5\%$ , $\leq 50\%$	$\geq 10\%$ , $\leq 30\%$	$\geq 15\%$ , $\leq 25\%$	
units of (d)		$\leq 15\%$	$\leq 10\%$	$\leq 5\%$ 0%
units of (e)–(m)		$\leq 15\%$	$\leq 10\%$	$\leq 5\%$ 0%

In case of imparting detergency, it is preferred to use monomer (k) [preferably (k112) and (k121) particularly DMAEM, DEAEM, MOEM and acrylates corresponding thereto] in an amount of at least 0.1%, particularly at least 0.5%.

#### PROPERTIES OF COPOLYMER (A)

Copolymers (A) are generally soluble at least 0.5 parts by weight (hereinafter referred to as pbw), preferably at least 2 pbw, more preferably at least 30 pbw, especially at least 70 pbw in 100pbw of mineral oil at 25°C.

In general, copolymers (A) have an Mw, as measured by gel permeation chromatography (GPC) using calibration curve of polystyrene, of at least 3,000 and not higher than 1,000,000. In view of imparting shear stability, copolymers (A) preferably have an Mw within such ranges as follows, which may vary depending upon kinds of oils and objects of addition of (A).

Oil	preferably	more preferably	particularly
Engine oil	$\geq 100,000$	$\geq 150,000$ , $\leq 1,000,000$	$\geq 200,000$ , $\leq 600,000$
ATF*, belt-CVTF**, and gear oil	$\geq 5,000$ , $\leq 100,000$	$\geq 8,000$ , $\leq 50,000$	$\geq 10,000$ , $\leq 35,000$ , espe- cially $\leq 20,000$
Hydraulic oil	$\geq 5,000$ , $\leq 400,000$	$\geq 8,000$ , $\leq 150,000$	$\geq 10,000$ , $\leq 100,000$

(Note) \*: automatic transmission fluid

\*\*: belt-continuously variable transmission fluid

Copolymers (A) have an SP value, as determined by the Fedors method [Polym. Eng. Sci. 14 (2) 152, (1974)], within the range of generally 8.6–11, preferably 9.2–10.5, particularly 9.4–9.8, in view of oil solubility and VI-improving ability.

Copolymers (A) preferably have an HLB of 0.5–7, particularly 1–6.5, more particularly 1.5–6, in view of de-emulsibility. HLB in this invention is Oda's HLB, defined based on a general concept of organic and inorganic natures of organic compounds ("New Introduction to Surface Active Agents" T. FUJIMOTO, SANYO CHEMICAL INDUSTRIES, LTD., pages 197–201).

#### PREPARATION OF COPOLYMER (A)

Copolymers (A) can be prepared by known polymerization methods, for instance, solution polymerization, bulk polymerization, emulsion polymerization and suspension polymerization. Polymerization is usually carried out in the presence of a polymerization catalyst, with or without a chain transfer agent.

Suitable polymerization catalysts include, for example, azo catalysts, such as 2,2'-azobisisobutyro-nitrile, 2,2'-azobis(2-methyl)butyronitrile, 2,2'-azobis-(2,4-dimethylvaleronitrile) (hereinafter referred to as ADVN) and dimethyl 2,2-azobisisobutyrate; and peroxide catalysts, such as t-butyl peroxypropionate, t-hexyl

peroxy-pivalate, t-butyl peroxyneohexanoate, t-butyl peroxy-neodecanoate, t-butyl peroxy-2-ethylhexanoate, t-butyl peroxyisobutyrate, t-amyl peroxy-2-ethylhexanoate, 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate, dibutyl peroxy-trimethyladipate, benzoyl peroxide, cumyl peroxide and lauroyl peroxide.

Exemplary of suitable chain transfer agents are C<sub>2</sub>-20alkyl mercaptans, such as dodecyl mercaptan (hereinafter referred to as Dm); C<sub>2</sub>-20mercaptoalkanoic acids, such as mercaptoacetic acid and mercaptopropionic acid; and C<sub>2</sub>-20(polyoxy)alkylene dithiols, such as 1,4-butanedithiol and triethylene glycol dimercaptan.

It may be desirable to carry out polymerization within a solvent, that is, through solution polymerization. Illustrative of suitable solvents are alcohol solvents, for example, C<sub>3</sub>-8alkanols, such as 2-propanol, 1-butanol and 2-butanol; hydrocarbon solvents, for example, aromatic solvents (aromatic C<sub>6</sub>-15hydrocarbons, such as benzene, toluene, xylene, ethylbenzene, C<sub>9</sub>-15alkylbenzenes, trimethylbenzene, ethyltoluene and mixtures of them), (cyclo) aliphatic C<sub>6</sub>-18hydrocarbon such as hexane, heptane, cyclo hexane and octane, mineral oils (such as paraffinic oils, naphthenic oils, solvent-refined oils, isoparaffin-containing high VI oils and hydrocracked high VI oils), and synthetic hydrocarbon lubricants (such as poly-a-olefin synthetic lubricants); ketone solvents, such as butanone and methyl ethyl ketone; and ester solvents, including, fatty oils, and synthetic ester lubricants, for example, di-C<sub>4</sub>-12alkyl C<sub>4</sub>-12dicar-boxylates, such as dioctyl sebacate and dioctyl adipate, polyol poly-C<sub>4</sub>-12alkanoates, such as pentaerythritol tetra-caproate; and tri-C<sub>4</sub>-12hydrocarbyl phosphates, such as tri-2-ethylhexyl phosphate, dibutyl phenyl phosphate, di-2-ethylhexyl phenyl phosphate, 2-ethylhexyl diphenyl phosphate and tricresyl phosphate) and combination of them. Preferred are alcohol solvents, particularly 2-propanol.

In carrying out solution polymerization, it is preferred to use monomers, a polymerization catalyst and optionally a chain transfer agent, at concentrations of 40-95% (particularly 60-90%), 0.1-5% (particularly 0.15-0.8%) and 0-5% (particularly 0-3%),

respectively, based on the weight of the polymerization mixture.

Polymerization is carried out preferably at a temperature of 50–140°C, particularly 60–120°C.

Polymerization of monomers can be done by random copolymerization or alternating copolymerizaton. Besides, graft copolymerization or block copolymerization may be employed. Preferred is random copolymerization.

Copolymers (A) having a prescribed Mw, SP and HLB can be obtained by adequate selection of polymerization conditions. For instance, Mw can be adjusted by polymerization temperature, and quantities (concentrations) of monomers, solvent, catalyst and chain transfer agent. SP can be adjusted by selection of kinds (such as alkyl chain length) and molar ratio of monomers calculated from SP of each constituent monomer (determined by Fedors method). For example, polymers of smaller SP can be obtained by using larger amount of monomer(s) having an alkyl group of longer chain length.

## VII and VII CONCENTRATE

VI improvers of this invention can be solvent-free or may be in the form of concentrate (or solution in a solvent). VII concentrates are preferred, because of being easily dissolved into oils.

VII concentrates include ones produced by solution polymerization and ones prepared by dissolving a polymer into a diluent.

Examples of suitable diluents include solvents as mentioned above, such as alcohol solvents, aromatic solvents and mineral oils; and (cyclo)aliphatic C<sub>6–18</sub> hydrocarbons, such as hexane, heptane, cyclohexane, octane, decalin and kerosene. Among these, preferred are (cyclo)aliphatic C<sub>6–18</sub>hydrocarbon lubricants and particularly mineral oils.

VII concentrates preferably contains copolymer (A) in a concentration of 20–

90%, particularly 30–85%, more particularly 40–80%, and a diluent in an amount of 10–80%, particularly 15–70%, more particularly 20–60%.

## LUBE OIL COMPOSITION

Base oils, into which VII according to the present invention is added, are not particularly limited.

Base oils preferably have a kinematic viscosity (hereinafter referred to as KV) of 1–18 mm<sup>2</sup>/s, particularly 2–15 mm<sup>2</sup>/s, at 100°C.

Base oils preferably have a VI of at least 60 (particularly at least 100, more particularly 105) and 180 or less (particularly 170 or less).

Base oils preferably have a pour point (defined in JIS K2269) of -5°C or less, particularly -10°C or less, and preferably at least -70°C, in view of low-temperature viscosity behavior, with little wax deposition at low temperature.

Suitable base oil includes, for example, mineral oils, as mentioned above as the solvent for polymerization. Among these, preferred are high VI oils, particularly isoparaffin-containing high VI oils and hydrocracked high VI oils.

Suitable lube oils include, for example, gear oils such as differential oils and industrial gear oils; transmission fluids such as manual transmission fluid (MTF), ATF and belt-CVT; traction oils such as troidal-CVT; hydraulic oils such as shock-absorber oils, power steering oils and industrial hydraulic oils; and engine oils (oils used in engines such as an engine for means of transportation and engine for machine tools).

In general, lube oil compositions contain added thereto copolymer (A) according to this invention in an amount of 0.01–45%. For use as VII, it is preferred to add (A) to oils in an amount of at least 1%, more preferred at least 5%, particularly at least 8%. For use as pour point depressant, the amount of (A) may be 0.01–3%.

Properties (such as viscosity) of base oils and content of (A) added thereto may vary depending upon uses and requirements of lube oils and addition purpose of

(A). Preferable ranges of kinematic viscosity (hereinafter referred to as KV) at 100°C of base oils and content of (A) based on lube oil compositions are as follows:

	<u>Engine oil</u>	<u>Gear oil and differential oil</u>	<u>ATF and belt-CVTF</u>	<u>Traction oil</u>	<u>Hydrau- lic oil</u>
(A), %	0.5–15	2–40	2–35	0.5–15	0.5–25
KV, mm <sup>2</sup> /s	3–10	3–18	2–6	1–5	1–10

Lube oil compositions containing copolymers (A), may further contain one or more other alkyl (meth)acrylate copolymers [hereinafter referred to as copolymers (B)] than copolymer (A).

Copolymers (B) are copolymers of two or more monomers selected from the group consisting of (a), (b), (c), (d) and (e)–(m) as mentioned above: including ones having units of one or more of monomers (a), (b) and (c) in an amount of less than 5%; ones having units of one of (a) and (b) in an amount of higher than 90%; ones having units of (c) in an amount of higher than 50%; and ones having units of (d) in an amount of higher than 15%. Suitable copolymers (B) include, for example, (B1) copolymers of two or more monomers (b), and (B2) copolymers of at least one monomer (b) and at least one monomer (c).

Copolymers (B) preferably contain units of (b) in an amount of 60–100% (particularly 65–100%) and units of (c) in an amount of 0–40% (particularly 0–35%).

Copolymers (B1) are preferably comprised of units of C<sub>12–18</sub>alkyl (meth)acrylates. Alkyl groups in alkyl (meth)acrylates constituting (B) have average carbon atom numbers (hereinafter referred to as C<sub>av</sub>) of 12 to 16.

It is preferred that copolymers (B) are mainly comprised of straight-chain alkyl (meth)acrylate units, and may contain branched-alkyl (meth)acrylate units in a minor amount of 0–30%.

Illustrative of copolymers (B1) and (B2) are copolymers of DDM/ODM (60–90%/10–40%, C<sub>av</sub>: 12.5–14.0), of DDM/HDM (50–90%/10–50%, C<sub>av</sub>: 12.3–13.8), of

DDM/TDM (30–90% /10–70%, C<sub>av</sub>:12.2–13.4) and of DDA/DDM (10–40%/10–40%, C<sub>av</sub>:12.0), and copolymers of DDM/TDM/HDM/MMA (20–45%/20–45%/0–20%/0.2–20%, C<sub>a</sub>:8.1–13.5), respectively.

Copolymers (B) preferably have an Mw of 5,000–1,000,000, particularly 10,000–250,000.

Copolymers (B) can be prepared by the same method as mentioned above for preparation of (A), and may be used in the form of concentrates in the same manner as (A).

Copolymers (A) and (B) may be added to a base oil separately or as a mixture of them.

Lube oil compositions can contain copolymers (A) and (B) added thereto in an amount of 0.5–45% in total. Preferable ranges of the total amount of (A) and (B) are 0.5–15% (engine oil and traction oil), 2–40% (gear oil), 2–35% (ATF) and 0.5–25% (hydraulic oil).

Copolymers (A) and (B) are preferably used in a weight ratio of at least 70/30, particularly 80/20–99.9/0.1, more particularly 90/10–99.9/0.1, in view of providing oils of lower viscosity at lower temperature.

Lube oil compositions containing said polymer (A) or said polymers (A) and (B), may further contain optionally one or more other additives.

Such additives include ones usually used in lube oils. Suitable additives include 1) detergents, for example, basic or overbased, or neutral metal salts, such as overbased alkali or alkaline earth metal salts of sulfonates (petroleum sulfonates, alkylbenzene sulfonates, alkynaphthalenesulfonates and the like), phenates, naphthenates, salicylates, carbonates, phosphonates, and mixtures of two or more of them; 2) dispersants, such as succinimides (bis- and mono- polybutenylsuccinimides and the like), Mannich dispersants and borates; 3) anti-oxidants, such as hindered phenols and secondary aromatic amines; 4) friction modifiers, for example, long chain fatty acids and esters thereof (such as oleic acid and oleates), long chain amines and

amides thereof (such as oleylamine and oleylamide); 5) antiwear agents, for example, molybdenum and zinc compounds (such as molybdenum dithiophosphate, molybdenum dithio carbamate and zinc dialkyl dithiophosphate); 6) extreme-pressure agents, for example, sulfur compounds (such as mono- and di-sulfides, sulfoxides and sulfur phosphide compounds), phosphide compounds, and chlorine compounds (such as chlorinated paraffins); 7) antifoam agents, such as silicone oils, metallic soaps, fatty acid esters and phosphate compounds; 8) demulsifying agents, for example, quaternary ammonium salts (such as tetraalkyl ammonium salts), sulfated oils, phosphates (such as phosphates of polyoxyethylene-containing nonionic surfactants); and 9) corrosion inhibitors, for example, nitrogen compounds (such as benzotriazole and 1,3,4-thiodiazoyl-2,5-bis dialkyl dithiocarbamate).

These additives 1)–9) can be used in such amounts as follows:

Additives	1),%	2),%	3),%	4),%	5),%	6),%	7),ppm	8),%	9),%
usually	0–20	0–20	0–5	0–5	0–5	0–20	2–1000	0–3	0–3
preferably	0.1–10	2.0–10	0.1–3	0.1–1	0.1–3	1.0–10	10–700	0–1	0–2

## EXAMPLES

Having generally described the invention, a more complete understanding can be obtained with reference to certain specific examples, which are included for purposes of illustration only and are not intended to limit the scope of the present invention.

Measuring methods and conditions are as follows:

(1) Mw, measured by GPC under the following conditions:

Apparatus: HLC-802A, produced by Tosoh Corp.;

Column: TSKgel-GMH6, produced by Tosoh Corp., two columns being connected in series; Column Temperature: 40°C;

Sample solution: 0.5 % tetrahydrofuran solution;

Injection amount: 200 micro L;

Detector: a refractive index detector;

Standard: polystyrene, TSK STANDARD POLYSTYRENE, produced by Tosoh Corp.

Data processor: SC-8020, produced by Tosoh Corp.

(2) Viscosity, measured at -40°C according to JPI-5S-26-85.

(3) VI, measured in accordance with JIS-K-2283.

(4) Shear stability, measured according to CEC L45-45-A-99, for test period of 20 hours.

Examples 1-7 and Comparative Examples 1-3:

(Production of Polymers A1 – A7 and B1 – B3)

Into a reaction vessel equipped with a stirrer, a heating and cooling device, a thermometer, a dropping funnel and a nitrogen inlet tube, 25pbw of IPA as solvent for polymerization was charged and heated to 85°C within an atmosphere of nitrogen. While maintaining the temperature within 70–85°C, a mixture of 1.5pbw of Dt, 0.5pbw of ADVN, 6pbw of IPA and monomers as written in Table 1, were added thereto dropwise from the dropping funnel over 2 hours in the absence of air. The reaction mixture was held for 2 hours at 85°C to complete polymerization, followed by distilling off IPA under reduced pressure for 3 hours at 85–120°C to obtain Polymers A1 to A7 and B1 to B3, having properties as shown in Table 1.

Comparative Example 4:

(Production of Polymer B4)

Polymer B4 having properties as shown in Table 1 was prepared in the same manner as in Example 1, except that toluene was used instead of IPA as the solvent for polymerization and Dt was used in amount of 0.4pbw.

Table 1

	Example							Comparative Example			
	1	2	3	4	5	6	7	1	2	3	4
Polymer No.	A1	A2	A3	A4	A5	A6	A7	B1	B2	B3	B4
Monomer, pbw											
(a) D-TM	50	30	-	-	20	50	50	-	-	-	-
(a) O-DM	-	-	30	50	20	-	-	-	-	-	-
(b1) DDM	-	-	-	-	-	-	-	-	-	-	80
(b1) TDM	31	51	52	22	10	41	31	80	60	31	-
(b1) HDM	-	-	-	6	22	-	-	2	10	-	-
(b2) ODM	-	-	-	3	9	-	-	-	15	-	20
(c1) HEMA	19	19	18	18	19	-	-	-	15	19	-
(c2) AAm	-	-	-	-	-	9	-	-	-	-	-
(c3) MAA	-	-	-	-	-	-	19	-	-	-	-
(d1) MMA	-	-	-	-	-	-	-	18	-	-	-
(d3) M-NM	-	-	-	-	-	-	-	-	-	50	-
Mw × 10 <sup>4</sup>	2	2	2	2	2	2	2	2	2	2	5
SP	9.6	9.6	9.6	9.6	9.6	9.4	9.4	9.1	9.5	9.6	9.0
HLB	3.2	3.4	3.4	3.2	3.4	3.1	4.1	2.5	3.1	3.4	1.9

Examples 8–14 and Comparative Examples 5–7:

(VII Concentrates and Lube Oil Compositions)

Into 35 pbw of a mineral oil (solvent-refined oil having a KV of 2.3 mm<sup>2</sup>/s at 100°C), was dissolved 65 pbw of each of Polymers A1 – A7 and B1 – B4 to prepare Concentrates CA1 – CA7 and CB1 – CB4, respectively.

Into a stainless steel vessel equipped with a stirrer, was charged 0.3 pbw of Concentrate CB4, followed by adding thereto a base oil (having a KV of 4.6 mm<sup>2</sup>/s at

100°C, a VI of 118 and a pour point of -17.5°C) and each of Concentrates CA1 – CA7 and CB1 – CB3, in such an amount providing a lube oil composition of a KV in the range of  $14.3 \pm 0.2$  mm<sup>2</sup>/s at 100°C as written in Table 2 to prepare 100pbw of lube oil compositions, having KV (mm<sup>2</sup>/s at 100°C), VI, low temperature viscosity (mPa·s at -40°C) and shear stability (%) as given in Table 2.

Table 2

	Example							Comparative		
	8	9	10	11	12	13	14	5	6	7
Polymer	A1	A2	A3	A4	A5	A6	A7	B1	B2	B3
Concen-	CA1	CA2	CA3	CA4	CA5	CA6	CA7	CB1	CB2	CB3
trate, pbw	45	45	43	44	44	44	47	35	41	41
KV, mm <sup>2</sup> /s	14.3	14.3	14.2	14.5	14.3	14.4	14.5	14.3	14.3	14.3
VI	216	215	206	209	212	197	212	175	200	213
Low temperature Viscosity, mPa·s, $\times 10^3$	52	90	90	80	75	100	100	>400	>400	>400
Shear sta- bility, %	3.5	3.6	3.9	4.0	3.8	4.5	4.0	7.0	4.8	4.0